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THERMAL STUDIES ON SOLID 2-CHLOROBENZYLIDENEPYRUVATE OF LIGHTER TRIVALENT LANTHANIDES

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Solid compounds of general formula LnL_3 for La and Ce and $LnL_3 \cdot nH_2O$ for Pr, Nd and Sm where *Ln* stands for trivalent lanthanides, *L* is 2-chlorobenzylidenepyruvate and n=2, 3 and 2 respectively, have been synthesized.

On heating these compounds decompose in two or five steps. They lose the hydration water in the first step and the thermal decomposition of the anhydrous compounds occurs with the formation of the respective oxide, CeO_2, Pr_6O_{11} and Ln_2O_3 (*Ln*=La, Nd, Sm) as final residue. The dehydration enthalpies found for these compounds (Pr, Nd and Sm) were: 140.1, 148.2 and 221.3 kJ mol^{-1}, respectively.

Keywords: *2-chlorobenzylidenepyruvate, lighter lanthanides, thermal behaviour*

Introduction

Several metal-ion complexes of phenyl-substituted derivatives of benzylidenepyruvate, (C_6H_5–CH=CH–$COCOO^-$ (BP)), have been investigated in aqueous solutions [1–5]. These works reported the thermodynamic stability (β_1), and spectroscopic parameters (ε_{1max}, λ_{max}), associated with 1:1 complex species, as well as analytical applications of sodium 4-dimethylamino-BP for gravimetric determination of Cu(II), or as indicator in the complexometric titrations of Th(IV) and Al(III), with EDTA.

The works reported the synthesis and investigation of the compounds by means of thermogravimetry, derivative thermogravimetry (TG, DTG), differential thermal analysis (DTA), X-ray powder diffractometry, and other methods of analysis. Establishment of stoichiometry and the details of the thermal decomposition were the main purposes of these studies [6–15].

In the present paper, solid compounds of lanthanum and lighter trivalent lanthanides (i. e. Ce, Pr, Nd and Sm) with 2-chlorobenzylidenepyruvate (2-Cl-BP) were prepared.

The compounds were investigated by means of complexometry, X-ray powder diffractometry, energy dispersive X-ray microanalysis (EDX), elemental analysis (EA), infrared spectroscopy, differential scanning calorimetry (DSC) and simultaneous thermogravimetry-differential thermal analysis (TG-DTA). The results allowed us to acquire information concerning these compounds in the solid state, including their thermal stability and thermal decomposition.

Experimental

Sodium 2-chlorobenzylidenepyruvate and its corresponding acid were synthesized and purified as follows: an aqueous solution of sodium pyruvate (22 g per 50 mL) was dropwise, with continuous stirring, to an aqueous solution of 2-chlorobenzaldehyde (29 g). Sixty milliliters of an aqueous sodium hydroxide solution (18% *m*/*v*) was slowly added while the reacting system was stirred and cooled in an ice-bath. The rate of addition of alkali was regulated so that the temperature remained between 5 and 9ºC. The formation of a pale yellow precipitate was observed during the addition of the sodium hydroxide solution.

The system was left to stand for ca. 3 h at room temperature (23–28ºC). The pale yellow precipitate (impure sodium 2-chlorobenzylidenepyruvate) was filtered, washed with five 100 mL portions of methanol, to remove most of the unreacted aldehyde and by-products was dissolved in water (500 mL) and aldehyde yet present as contaminating was removed through a separator funnel.

Concentrated (12 mol L^{-1}) hydrochloric acid was added under continuous stirring to sodium 2-chlorobenzylidenepyruvate solution until total precipitation of 2-chlorobenzylidenepyruvic acid (12.3 g).

Aqueous solutions of sodium 2-Cl-BP 0.1 mol L^{-1} were prepared by direct weighing and dissolution of the salt. Lanthanide chlorides were prepared from the corresponding metal oxides (except for cerium) by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness, the residues redissolved in distilled water and the solutions again evaporated to near dryness to eliminate the ex-

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Table 1 Analytical data for *Ln* $(L)_3 \cdot nH_2O$

Compound	Water/%		*L* lost/%		Metal/%			Cl lost/%		Carbon/%		Hydrogen/%	
	theor.	TG	theor.	TG	theor.	TG	EDTA	theor.	TG	theor.	EA	theor.	EA
$La(L)_3$	–	–	78.78	78.55	18.09	18.29	18.13	3.58	3.73	46.93	46.87	2.37	2.46
$Ce(L)_3$	–	–	77.62	77.61	18.22	18.23	17.55	–	–	46.86	46.50	2.36	2.48
$Pr(L)_3 \cdot 2H_2O$	4.47	4.52	74.40	74.75	17.48	17.16	17.15	2.74	2.35	44.71	44.50	2.76	2.59
$Nd(L)_3 \cdot 3H_2O$	6.54	6.39	73.12	73.54	17.44	17.21	17.12	3.32	3.38	43.56	43.73	2.93	2.80
$Sm(L)_3 \cdot 2H_2O$	4.42	4.43	74.19	74.41	18.44	18.25	18.96	3.37	3.48	44.20	44.36	2.73	2.51

Ln – lanthanum or lanthanides; *L* – 2-chlorobenzylidenepyruvate

cess of hydrochloric acid. The residues were again dissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain ca. 0.1 mol L^{-1} solutions, whose pH were adjusted to 5.0 by adding diluted sodium hydroxide or hydrochloric acid solutions. Cerium(III) was used as its nitrate and ca. 0.1 mol L^{-1} aqueous solutions of this ion were prepared by direct weighing and dissolution of the salt.

The solid compounds were prepared by slowly adding, with continuous stirring, solutions of the ligand to the respective metal chloride or nitrate solutions, until total precipitation of metal ions. The precipitates were washed with distilled water in order to elimination of chloride (or nitrate) ions, filtered through and dried on Whatman nº 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

For analyzed complexes, hydration water, ligand and metal contents were determined from the TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solutions using xylenol orange as indicator [17].

X-ray powder patterns were obtained by using a Siemens D-5000 X-ray diffractometer, employing CuK_α radiation (λ=1.541 Å) and setting of 40 kV and 20 mA.

Infrared spectra for 2-Cl-BP (sodium salt) as well as for its trivalent lanthanide compounds were run on a Nicolet mod. Impact 400 FT-IR instruments, in the range of 4000–400 cm^{-1}. The solid samples were pressed into KBr pellets.

Carbon and hydrogen contents were determined by microanalytical procedures, with an EA 1110 CHNS-O Elemental Analyzer from CE Instruments.

Simultaneous TG-DTA and DSC curves were obtained with two thermoanalytical systems, models SDT 2960 and DSC 2010, both from TA instruments. The purge gas was an air with a flow rate of 100 mL min^{-1}. The heating rate was β=20 K min^{-1} and the sample masses were about 9 mg. Alumina and aluminum crucibles, the latter with perforated covers, were used for TG-DTA and DSC, respectively.

The residues of the thermogravimetric experiments were characterized by an energy dispersive X-ray microanalysis EDX system Noran.

Results and discussion

The analytical results of the synthesized compounds are shown in Table 1. These results permitted to calculate the stoichiometry of the compounds, which was in agreement with general formula $Ln(2\text{-}Cl\text{-}BP)_3$ (*Ln*=La, Ce), $Ln(2\text{-}Cl\text{-}BP)_3 \cdot nH_2O$, (*Ln*=Pr, Nd, Sm) and *n*=2, 3 and 2, respectively.

The X-ray powder patterns (Fig. 1) showed that all the compounds were obtained in crystalline state and with evidence for formation of an isomorphous series, except the samarium compound.

Infrared spectroscopic data of 2-chlorobenzylidenepyruvate (sodium salt) and its compounds with lanthanum and lighter trivalent lanthanides are shown in Table 2. The bands found for 2-Cl-BP (sodium salt) centered at 1682 cm^{-1} (ketonic carbonyl stretching) and 1615 cm^{-1} (antisymmetrical carboxylate vibration). These bands are shifted to lower frequencies in the compounds, namely, 1627–1668 and 1585–1592 cm^{-1}, re-

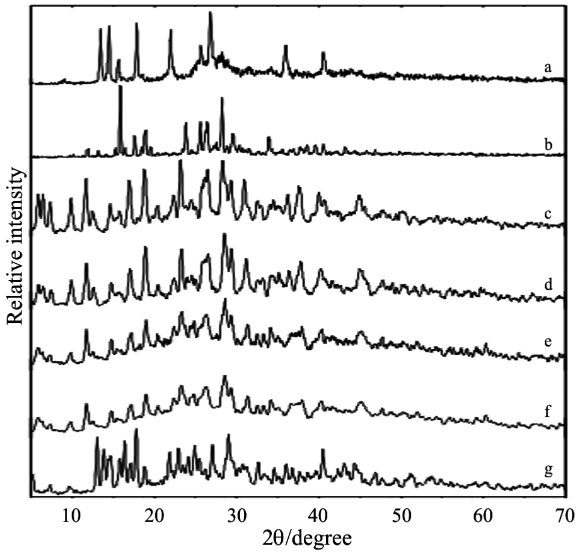

Fig. 1 X-ray powder diffraction patterns of a – 2-Cl-BP-Na·1.5H_2O, b – 2-Cl-BP-H·0.5H_2O, c – 2-Cl-BP-La, d – 2-Cl-BP-Ce, e – 2-Cl-BP-Pr·2H_2O, f – 2-Cl-BP-Nd·3H_2O and g – 2-Cl-BP-Sm·2H_2O

Table 2 Spectroscopic data for sodium 2-chlorobenzylidenepyruvate and for its compounds with lanthanum(III) and lighter trivalent lanthanides

Compounds	$\upsilon_{(O-H)}H_2O$	$\upsilon_{s(COO^-)}$	$\upsilon_{as(COO^-)}$	$\upsilon_{(C=O)}$
$NaL\cdot 1.5H_2O$	3443 m	1402 m	1615 s	1682 s
$La(L)_3$	–	1400 m	1592 s	1668 s
$Ce(L)_3$	–	1397 m	1591 s	1668 s
$Pr(L)_3\cdot 2H_2O$	3436 m	1409 m	1591 s	1637 s
$Nd(L)_3\cdot 3H_2O$	3489 m	1413 m	1585 s	1627 s
$Sm(L)_3\cdot 2H_2O$	3427 m	1390 m	1586 s	1635 s

L – 2-chlorobenzylidenepyruvate; s – strong; m – medium; $\upsilon_{as(O-H)}$ – hydroxyl group stretching frequency; $\upsilon_{s(COO^-)}$ and $\upsilon_{as(COO^-)}$ – symmetrical and antisymmetrical vibrations of the COO^- structure; $\upsilon_{s(C=O)}$ – ketonic carbonyl stretching frequency

spectively, suggesting lanthanum and lanthanides coordination by α-ketonic carbonyl and carboxylate groups of used ligand [18, 19]. This finding is in agreement with the observed behaviour in compounds of some bivalent metal ions and lanthanides with other phenyl substituted derivatives of BP [12, 14, 15].

The simultaneous TG-DTA curves of the same analyzed compounds are shown in Fig. 2. These curves

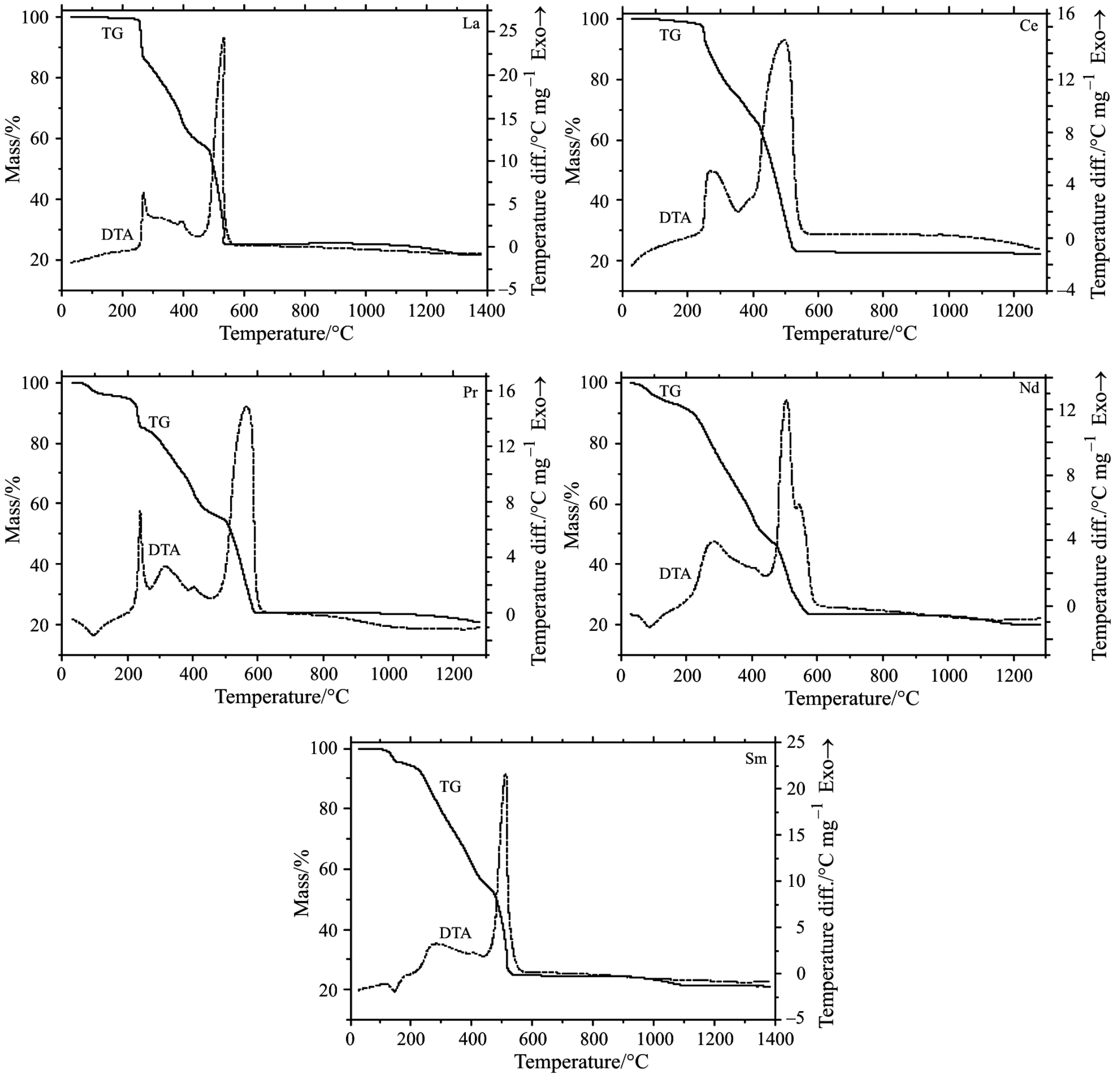

Fig. 2 TG-DTA curves of the compounds: $La(2\text{-}Cl\text{-}BP)_3$ (*mi*=8.802 mg); $Ce(2\text{-}Cl\text{-}BP)_3$ (8.507 mg); $Pr(2\text{-}Cl\text{-}BP)_3\cdot 2H_2O$ (9.244 mg); $Nd(2\text{-}Cl\text{-}BP)_3\cdot 3H_2O$ (8.928 mg) and $Sm(2\text{-}Cl\text{-}BP)_3\cdot 2H_2O$ (8.422 mg)

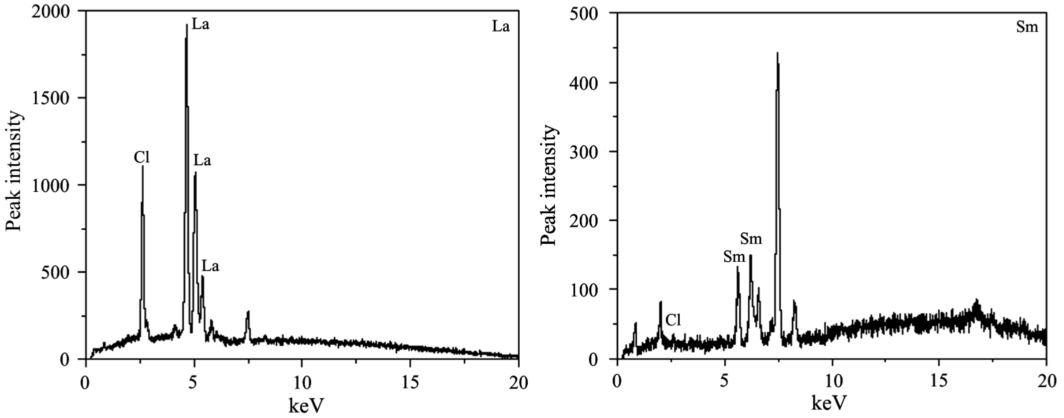

Fig. 3 EDX data of the thermal decomposition residues up to 700°C

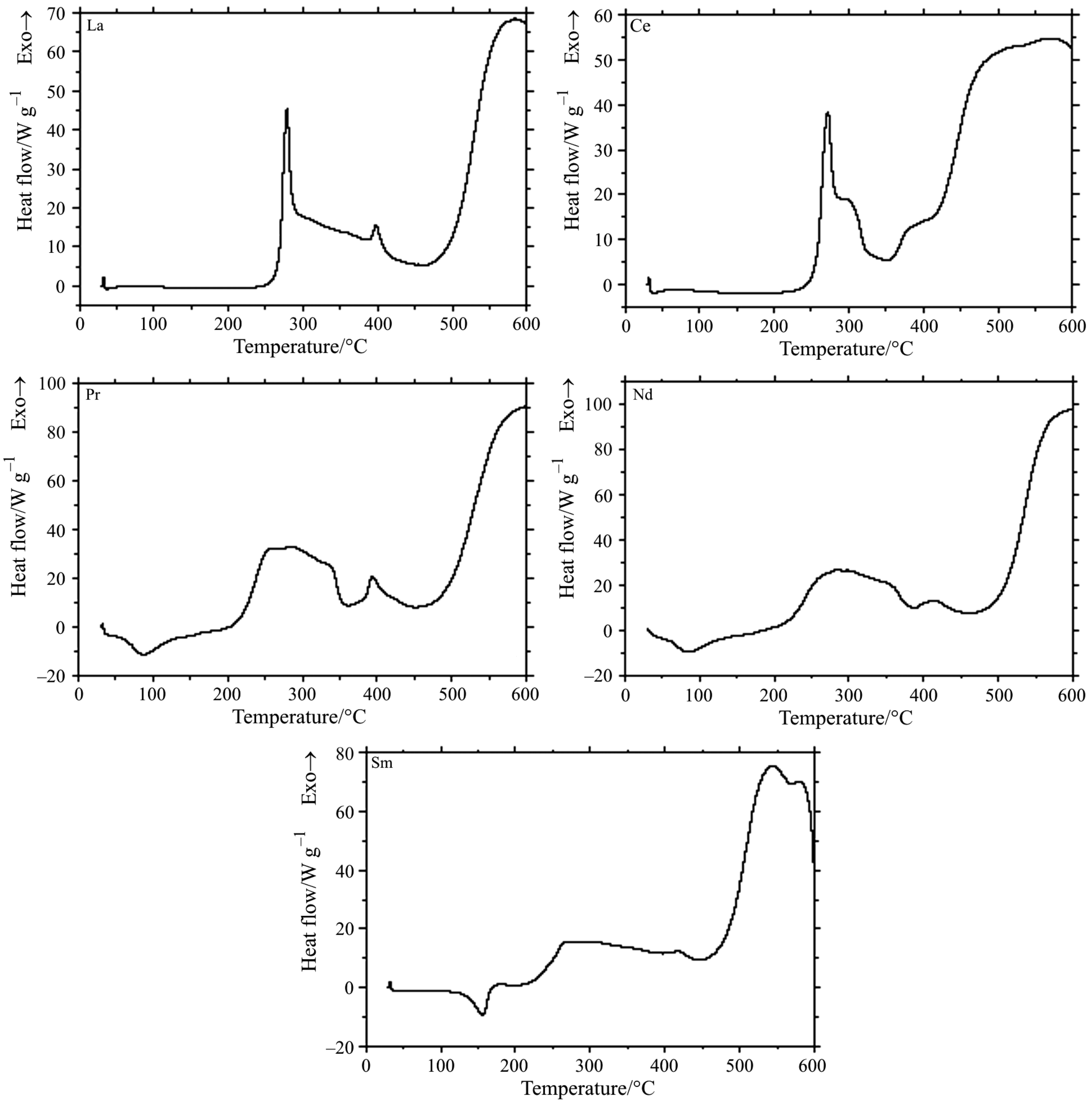

Fig. 4 DSC curves of the compounds: La(2-Cl-BP)$_3$ (*mi*=2.2 mg); Ce(2-Cl-BP)$_3$ (2.3 mg); Pr(2-Cl-BP)$_3$·2H$_2$O (5.3 mg); Nd(2-Cl-BP)$_3$·3H$_2$O (5.1 mg) and Sm(2-Cl-BP)$_3$·2H$_2$O (2.4 mg)

exhibit mass losses in two (Ce), four (La, Nd, Sm) and five (Pr) steps and thermal events corresponding to these losses.

The first mass loss between 40–120ºC for praseodymium and neodymium and 90–150ºC for samarium compounds is attributed to dehydration, which occurs in a single step. After dehydration, the observed mass losses for all compounds are due to the thermal decomposition of anhydrous compounds. These take place in consecutive and/or overlapping steps with partial losses which are characteristic for each compound.

For cerium compound, the thermal decomposition occurs up to 540ºC with the formation of cerium(IV) oxide CeO_2 as final residue. The thermal stability of the cerium compound is in a disagreement with the other cerium compounds have been already studied [6, 7, 12].

For the other compounds, the mass losses up to 540ºC (La), 600ºC (Pr), 590ºC (Nd) and 550ºC (Sm), corresponding to exothermic peaks, are attributed to the oxidation of the organic matter, with the probable formation of lanthanide oxychloride, accompanied by small quantities of carbonaceous residue. The residue of the samples formed after their heating up to 540ºC (La), 600ºC (Pr), 590ºC (Nd) and 550ºC (Sm) was dissolved in nitric acid. $AgNO_3$ adding to these solutions indicated the presence of chloride ions. The presence of chloride ions in these residues was also verified by EDX investigations (Fig. 3). The EDX data also show that the presence of chloride ions decrease with the increase of the atomic number of the lanthanides as already observed for the heavy trivalent lanthanides compounds with the 4-chlorobenzylidenepyruvates [14]. The X-ray powder patterns showed that the residue up to this temperature is a mixture of the respective metal oxide and oxychloride in no simple stoichiometric relation.

The last step between 1050–1320ºC (La), 1000–1280ºC (Pr), 900–1200ºC (Nd) and 860–1100ºC (Sm) is due to the thermal decomposition of the lanthanide oxychlorides to the respective oxide, Pr_6O_{11} and Ln_2O_3 (*Ln*=La, Nd and Sm), as proven by their X-ray powder diffraction patterns, compared to those associated with the corresponding authentic oxides.

The DSC curves of the compounds are shown in Fig. 4. These curves show endothermic and exothermic peaks that all are in accordance with the mass losses observed in the TG curves. The endothermic peak at 90ºC, for praseodymium and neodymium, and 150ºC for samarium compounds is assigned to the dehydration. The dehydration enthalpies found for these compounds (Pr, Nd and Sm) were 140.1, 148.2 and 221.3 kJ mol^{-1}, respectively. These results are in agreement with the dehydration temperature observed in the TG-DTA and DSC curves of these compounds. The higher enthalpy as well as the dehydration temperature for the samarium compound than in the praseodymium and neodymium compounds is due to the strongly bond water.

The mass losses, temperature ranges and the peak temperatures observed in each step in the TG-DTA curves are shown in Table 3.

Table 3 Temperature ranges θ (degree), mass losses (%) and peak temperatures observed for each step of the TG-DTA curves of the compounds. $Ln(L)_3 \cdot nH_2O$, where *Ln*=lanthanides, *L*=2-chlorobenzylidenepyruvate

Compound		Steps					Δm_T	
		First	Second	Third	Fourth	Fifth	theor.	TG
$La(L)_3$	θ/degree	115–280	280–425	425–540	1050–1320		78.78	78.55
	loss/%	15.05	24.52	35.25	3.73			
	peak/°C	275 (exo)	400 (exo)	535 (exo)				
$Ce(L)_3$	θ/degree	100–400	400–540				77.62	77.60
	loss/%	33.56	44.05					
	peak/°C	280 (exo)	495 (exo)					
$Pr(L)_3 \cdot 2H_2O$	θ/degree	50–120	120–245	245–440	440–600	1000–1280	78.87	79.27
	loss/%	4.52	10.86	27.68	32.86	3.35		
	peak/°C	100 (endo)	245 (exo)	320, 400 (exo)	560 (exo)			
$Nd(L)_3 \cdot 3H_2O$	θ/degree	40–120	120–440	440–590	900–1200		79.66	79.93
	loss/%	6.39	45.46	24.70	3.38			
	peak/°C	90 (endo)	280 (exo)	505 (exo) 550 (shoulder)				
$Sm(L)_3 \cdot 2H_2O$	θ/degree	90–150	150–425	425–550	860–1100		78.61	78.84
	loss/%	4.43	38.94	31.99	3.48			
	peak/°C	150 (endo)	290 (exo)	510 (exo)				

Δm_T – total mass losses calculated assuming that the find solid products of decomposition of the obtained complexes are oxides: CeO_2, Pr_6O_{11} and M_2O_3 (*M*=La, Nd, Sm).

Conclusions

Based on the TG curves, the results of elemental analysis and complexometric titration, a general formula could be established for the synthesized compounds.

TG-DTA and DSC experiments provided previously unreported information concerning the thermal behaviour and thermal decomposition of these compounds.

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References

1 C. B. Melios, V. R. Torres, M. H. A. Mota, J. O. Tognolli and M. Molina, Analyst, 109 (1984) 385.

2 C. B. Melios, J. T. S. Campos, M. A. C. Mazzeu, L. L. Campos, M. Molina and J. O. Tognolli, Inorg. Chim. Acta, 139 (1987) 163.

3 C. B. Melios, H. Redigolo and M. Molina, J. Inorg. Biochem., 36 (1989) 307.

4 C. B. Melios, M. Ionashiro, H. Redigolo, M. H. Miyano and M. Molina, Eur. J. Solid State Inorg. Chem., 28 (1991) 291.

5 R. N. Marques, M. Molina and M. Ionashiro, J. Alloys Compd., 249 (1997) 102.

6 L. C. S. Oliveira, C. B. Melios, C. A. Ribeiro, M. S. Crespi and M. Ionashiro, Thermochim. Acta, 219 (1993) 215.

7 M. H. Miyano, C. B. Melios, C. A. Ribeiro, H. Redigolo and M. Ionashiro, Thermochim. Acta, 221 (1993) 53.

8 D. E. Rasera, L. S. C. Oliveira, C. B. Melios and M. Ionashiro, Thermochim. Acta, 250 (1995) 151.

9 R. A. Mendes, M. A. S. Carvalho Filho, N. S. Fernandes, L. M. D'Assunção, C. B. Melios and M. Ionashiro, An. Asoc. Brás. Quim., 47 (1998) 329.

10 N. S. Fernandes, M. A. S. Carvalho Filho, C. B. Melios and M. Ionashiro, J. Therm. Anal. Cal., 59 (2000) 663.

11 E. Schnitzler, C. B. Melios and M. Ionashiro, J. Therm. Anal. Cal., 70 (2002) 581.

12 R. N. Marques, C. B. Melios and M. Ionashiro, J. Alloys Compd., 344 (2002) 88.

13 I. A. Petroni, F. L. Fertonani, C. B. Melios and M. Ionashiro, Thermochim. Acta, 400 (2003) 187.

14 N. S. Fernandes, M. A. S. Carvalho Filho, C. B. Melios and M. Ionashiro, J. Therm. Anal. Cal., 73 (2003) 307.

15 N. S. Fernandes, M. A. S. Carvalho Filho, R. A. Mendes, C. B. Melios and M. Ionashiro, J. Therm. Anal. Cal., 76 (2004) 193.

16 M. Reimer and M. Howard, J. Am. Chem. Soc., 50 (1928) 2506.

17 M. Ionashiro, C. A. F. Graner and I. Zuanon Netto, Ecl. Quim., 8 (1983) 29.

18 F. A. Cotton, The Infra-Red Spectra in Metal Complex in Modern Coordination Chemistry (J. Lewis and R. G. Wilkins, Eds), Interscience, New York. 1960, p. 379.

19 K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, Part B, 5th Ed., Wiley, New York 1997, p. 58.